# Pulsed field ionization photoelectron photoion coincidence spectroscopy using two-bunch and 'dark-gap' multi-bunch synchrotron radiation at the Advanced Light Source

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## INTRODUCTION

Recently we have developed a scheme for measuring pulsed field ionization (PFI) photoelectron spectra (PFI-PE) of various molecules using two-bunch and multi-bunch synchrotron radiation at the Chemical Dynamics Beamline at the Advanced Light Source. Such detection schemes for PEs are far superior to conventional threshold photo-electron (TPE) measurements in terms of achievable resolution. Using our electron time-of-flight spectrometer, resolutions down to about 1.0 $cm^{-1}$ have been achieved which is roughly 8-10 times better that that achieved in similar TPE measurements.[1] A natural progression from PE measurements is PEPICO spectroscopy where parent and fragment ions of ionized species are collected in coincidence with energy selected electrons, producing mass analyzed spectra. The internal energy of the ions can thus be selected and fragmentation patterns can be determined state selectively. Plots of fractional abundance of all the product channels, called breakdown diagrams, can often be used to determine very precise onsets for ionic dissociations from which accurate heats of formation of fragment species can be derived. The accuracy of such diagrams is limited by the resolution in the PE measurement. The prospect of performing PFI-PEPICO measurements with resolutions far greater than TPE techniques is therefore an attractive one. Another advantage of examining the mass of fragments formed in PFI-PE spectroscopy is that contaminants present in samples can effectively be eliminated from the scans. One good example of an experiment where contaminants would be problematic is the study of radicals following photodissociation. Here PFI-photoelectrons from the parent species may complicate spectra and mass analysis would therefore alleviate these complications. PFI-PEPICO may also prove to be a useful technique for studying ion molecule chemistry at a rotational level. By performing PFI-PEPICO with two samples present in the reaction region at one time and determining the masses of the observed ions, the relative rates of reaction as a function of energy corresponding to the different excited levels of the photoexcited cation can be evaluated.

Here we present results on the PFI-PEPICO of $O_2$ performed using two-bunch and multi-bunch synchrotron radiation around its dissociation threshold and demonstrate resolutions of the order of 1meV.

## EXPERIMENT

Electrons and ions were extracted in opposite directions from the interaction region and electron discrimination was obtained by timing. Coincidence spectra were recorded using a multi-channel scalar with the electrons providing the start and the ions the stop. In the two-bunch experiments performed here, a DC field of between 0 and 2 V $cm^{-1}$ was maintained across the two plates that straddle the interaction region with a 6.95 V $cm^{-1}$ field pulse applied for 160 ns approximately 100 ns after each light pulse reached the interaction region. Since this high field PFI pulse was on for a good length of time (roughly half the total time in this case), it caused very efficient ion extraction. Collection efficiencies measured for the $Ar^+ {}^2P_{3/2}$ were 7.3% for the electron and 19.3% for the ions measured with zero volts DC across the interaction region. We performed PFI-PEPICO using multi-bunch synchrotron radiation by applying a 200 ns, 6.95 V $cm^{-1}$ PFI/extraction pulse across the interaction region ~ 10 ns after the last light pulse prior to a 144 ns dark gap. A DC field of 0.20 V $cm^{-1}$ was applied across the interaction region to clear the hot electrons prior to the PFI-pulse. This small field is necessary to sweep the hot electrons away and to ensure that the PFI-PE spectra are clean of autoionizing and direct ionization structures. Pulses of length greater than the dark gap are possible since the overlap is far removed (~130ns) from the PFI region and electrons from the first light bunches will therefore not interfere with our signal. Of course by overlapping the light, we will field ionize and lose any Rydberg states formed in the first set of bunches in the multi-bunch, but an overlap of around ~50 ns was found to have little effect on the PFI-PE signal levels. This indicates that the lifetime of the Rydberg states in this first region are too short to be detected in the present experimental arrangement. Therefore an overlapping pulse of 200 ns duration was used to aid ion extraction.

## RESULTS

PFI-PEPICO was performed on $O_2$ using both 2-bunch and multi-bunch synchrotron radiation. In the two-bunch mode we performed PFI-PEPICO scans on the $O_2^+$ b state from $v^+ = 5$ to 7 using a photon energy corresponding to the maximum intensity of the peaks observed in the PFI-PE spectra. The PFI-PEPICO TOF spectra recorded with a bin-width of 5 ns can be seen in Figure 1.

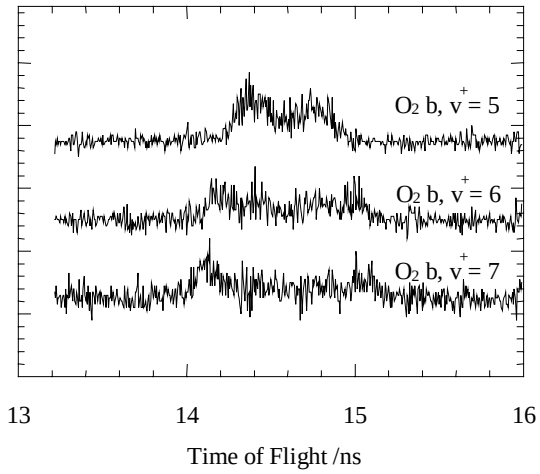


Figure 1. PFI-PEPICO TOF spectra for $O_2^+$ at energies corresponding to the b state $v^+ = 5$ to 7.

The dissociation limit is believed to occur at $v^+ = 4$, $N^+ = 9$.[3] The width of the peaks seen in Figure 1 reflect the kinetic energy released in dissociation which increases as the photon energy is increased. In our molecular beam sample we estimate that our rotational temperature is ~10K from a Buckingham-Orr-Sichel[2] (BOS) model of the $v^+ = 4$ branch performed on $O_2$ during multi-bunch. This temperature is too cold to allow population of the $N^+ = 9$ level, so the only way that we can observe $O^+$ at this vibration is from the effusive part of the beam.

Determination of the breakdown diagram over the $v^+ = 4$ band was therefore performed using an effusive sample and the data were taken in multi-bunch mode. PFI-PEPICO TOF spectra were taken in the energy region 18.713 to 18.726 eV and the areas under the $O_2^+$ and $O^+$ peaks were determined following background subtraction. The resulting breakdown diagram can be seen in Figure 2 where the filled circular symbols represent $O^+$ and the filled squares $O_2^+$. To obtain an accurate measure of the AE of $O^+$,

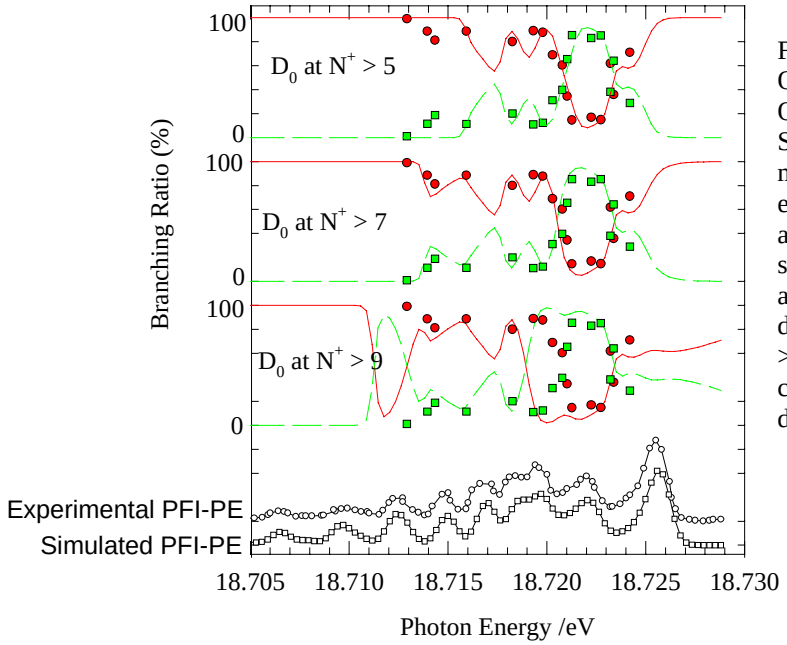


Figure 2. Branching ratio of $O_2^+/O^+$ (squares/circles) from $O_2$ at varying photon energies. Simulated (adjusted BOS model, see text ) and experimental PFI-PE spectra are also shown. From the simulation breakdown diagrams are calculated assuming the dissociation limit occurs at $N^+ > 5$, 7 and 9 and data are compared. (solid lines $O^+$, dashed $O_2^+$)

the PFI-PE spectrum was recorded under the same experimental conditions with 30 μm slits resulting in a resolution of ~ 1meV and a BOS simulation was performed on this spectrum. $B_{v+} = 1.175$ cm$^{-1}$ and $IE_{v+}=15.7224$ eV were used in the simulation and BOS coefficients $C_0$ and $C_2$ were set at 0.3 and 0.7, respectively. The fit was relatively poor in the region 18.717 to 18.722 eV and it was necessary to independently adjust the bands resulting in $N^+ = 7$, 9,11, 13 and 15 multiplying each by 0.34, 1.50, 1.36, 1.21 and 1.41 respectively. When this was performed, an excellent fit to the experimental data was obtained.

The reason for the poor fit using the BOS model we believe is caused by a lifetime effect that we have also observed in other molecules such as $CH_4$ and $C_2H_2$. Basically, the lifetime of $O^*$ is greater than $O_2^*$ at the dissociation limit as it is less prone to autoionization. An increase in the PFI-PE intensity is therefore observed as the

dissociation threshold is passed. A relative increase in the $N^+ > 7$ levels can therefore be explained. However for the best fit, the levels resulting in $N^+ = 7$ had to be decreased. This may indicate that the lifetime of the $O_2^*$ is decreased for some reason at this level or that some type of low-*n* Rydberg interaction is occurring. Once a good fit was obtained, then the three separate breakdown diagrams were calculated assuming that $N^+>5$, $N^+>7$ and $N^+>9$ rotational levels led to dissociation. Each of these simulated breakdown diagrams are shown in Figure 2 along with a duplicated set of experimental data. The dashed line represents $O_2^+$ and the solid line $O^+$. As can be seen, the $N^+ > 9$ simulation gives a poor fit in the region 18.718 to 18.721 eV, $N^+ > 5$ gives a poor fit in the region 18.712 to 18.716 eV with the $N^+ > 7$ simulation giving the best overall fit. This therefore agrees very well with previous findings on the dissociation limit[3] and demonstrates that PFI-PEPICO can now be performed with resolutions down to about 1 meV.

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